

The Integral Rate Equation of Pure Titanium in Nitric-Hydrofluoric Acid Solutions



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Abstract

Effects of immersion time, nitric or hydrofluoric acid concentration and solution temperatures on corrosion loss of titanium were investigated to obtain estimated equation of corrosion loss of titanium, integral (corrosion) rate equation, in mixed solutions of nitric and hydrofluoric acid. Corrosion loss of titanium was increased with immersion time and solution temperatures. It was also found that increased hydrofluoric acid solution enhanced corrosion loss, while effects of nitric acid concentration was not large. According to the studies above, corrosion loss of titanium was found to be approximately expressed as the following integral rate equation.

*$\log X \cong \log A' - \{E_a / (2.303RT)\} + m' \cdot \log C(\text{HF}) + n' \cdot \log C(\text{HNO}_3) + S \cdot \log t$
where X is corrosion loss ($\text{mol} \cdot \text{m}^{-2}$), R is gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), T is absolute temperature (K), $C(\text{HF})$ and $C(\text{HNO}_3)$ are concentration ($\text{mol} \cdot \text{kg}^{-1}$) of hydrofluoric acid and nitric acid in solutions respectively and t is immersion time (s). Mean values and confidence interval of 95% of constant, A' and coefficients E_a , m' , n' and S are as follows. $\log A' = 3.400 \pm 0.152$, $E_a = 33190 \pm 1273$, $m' = 0.926 \pm 0.027$, $n' = 0.042 \pm 0.025$, $S = 0.938 \pm 0.039$*

1. Introduction

Mixed aqueous solutions of nitric acid and hydrofluoric acid (hereinafter referred to as nitric-hydrofluoric acid solutions) are the most popular mixed acids that are industrially used for the descaling of stainless steel and titanium and are employed in large amounts for the etching of metallic materials in laboratories¹⁻⁴⁾. Their utilization value is very high, especially for titanium, because they provide a

high dissolution rate and low hydrogen absorption during pickling of titanium.

Many reports have been published about the corrosion behavior and corrosion mechanism of titanium in the nitric-hydrofluoric acid solutions⁵⁻⁷⁾. There are, however, no studies that have analyzed the corrosion behavior of titanium in the nitric-hydrofluoric acid solutions by considering the exothermic phenomenon that accompanies the dissolution of titanium in the nitric-hydrofluoric acid solution⁸⁾.

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There are no reports either that have derived integral rate equations that express as a function of the nitric acid concentration, hydrofluoric acid concentration, solution temperature and immersion time the corrosion loss (dissolution amount) that is important for the actual pickling and etching of titanium. This report has clarified a practical equation to estimate the integral corrosion rate of titanium by using an experimental technique capable of avoiding the heat generated in the solution by the dissolution of titanium in the solution.

2. Experimental Material and Methods

2.1 Materials

Grade 1 commercially pure titanium sheet was used as the specimen. Its chemical composition is 0.05 mass% C-0.071 mass% O-0.0016 mass% H-0.0094 mass% N-0.053 mass% Fe. Corrosion test specimens were machined from the sheet to a thickness of 4 mm, length of 25 mm and width of 25 mm, wet polished on all surfaces to #600, ultrasonically cleaned in acetone for about 600 s, dried, weighed, and corrosion tested.

2.2 Test solutions

Reagent grade nitric acid (purity: 61 mass%), reagent grade hydrofluoric acid (purity: 42 mass%), and distilled water were mixed and adjusted to produce nitric-hydrofluoric acid solutions with nitric and hydrofluoric acid concentrations of 0 to 3 mol · kg⁻¹, respectively.

2.3 Corrosion test

To clarify the integral rate equation of titanium in the nitric-hydrofluoric acid solution, specimens were immersed in 250 cm³ of the nitric-hydrofluoric acid solution in seven polyethylene corrosion test cells held at 298K, 308K, 323K and 333K±0.5K using a constant-temperature water tank for 60 to 780 seconds. Given the rise of the solution temperature with the progress of the corrosion reaction, the corrosion test cells into which the specimens were immersed were sequentially changed for the first 0-60 s and at intervals of 120 s thereafter. After each change, the specimens were washed with water, dried with cold air, and measured for weight loss to determine the change in the corrosion loss with the immersion time. To verify the validity of the integral rate equation derived from the experimental results, the corrosion loss of the specimens in various nitric-hydrofluoric solutions held at 313K±0.5K was also measured.

3. Experimental Results and Discussion

3.1 Immersion time dependence of corrosion loss

As example, Fig. 1 shows the effects of the nitric acid concentration, hydrofluoric acid concentration, and immersion time *t* on the corrosion loss *X* of titanium in the nitric-hydrofluoric acid solutions at a temperature of 323K. At each nitric acid concentration and hydrofluoric acid concentration, the corrosion loss almost linearly increased with increasing immersion time. When the immersion time was constant, the corrosion loss markedly increased with increasing hydrofluoric acid concentration, but the nitric acid concentration dependence of the corrosion loss was very small.

The relations between the corrosion loss and the immersion time shown in Fig. 1 are represented as double logarithmic plots by nitric acid concentration and hydrofluoric acid concentration in Fig. 2. At each solution temperature, hydrofluoric acid concentration, and nitric acid concentration, the logarithmic value of the corrosion loss of titanium linearly increases with respect to the logarithmic value of the immersion time. Here, the corrosion of titanium in the nitric-hydrofluoric solution is assumed to proceed by the following reaction⁶⁾:

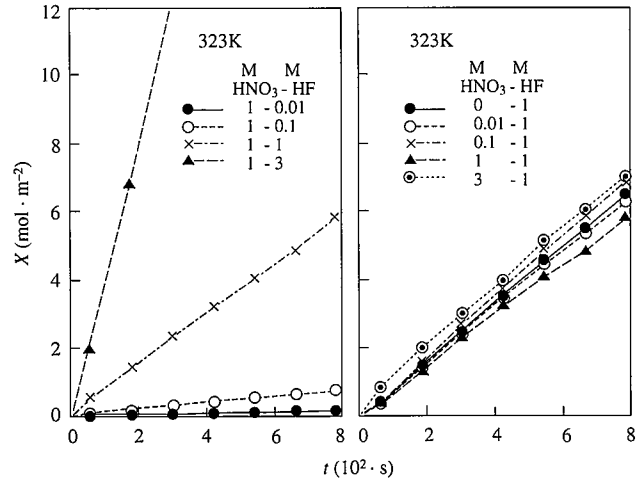


Fig. 1 Effects of HF concentration, HNO₃ concentration, and immersion time on corrosion loss *X* of titanium

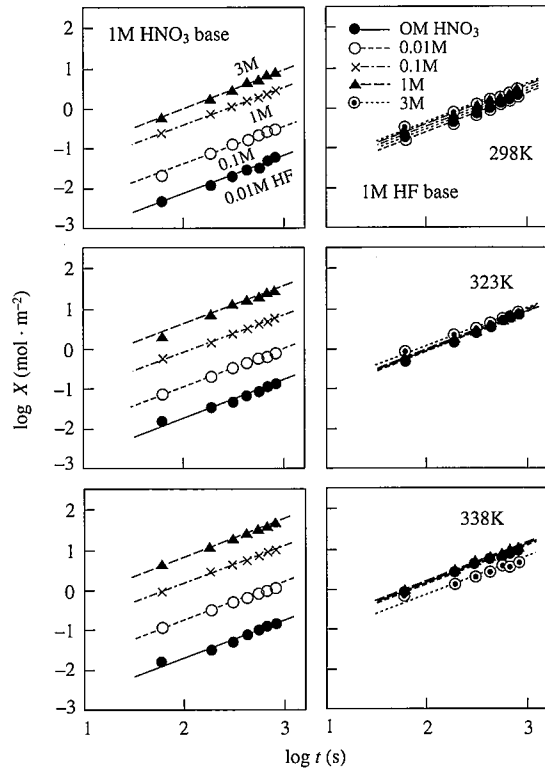
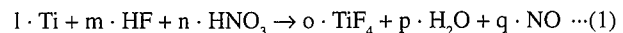


Fig. 2 Effect of immersion time on corrosion loss *X* of titanium in various HNO₃/HF solutions



The corrosion reaction rate (corrosion rate: *C.R.*) of the above form is generally given by the following equation⁸⁾:

$$C.R. = -da(\text{Ti}) / dt = k \cdot a(\text{Ti})^{l'} \cdot a(\text{HF})^{m'} \cdot a(\text{HNO}_3)^{n'} \dots(2)$$

where *k* is the rate constant of the corrosion reaction; *a*(Ti), *a*(HF) and *a*(HNO₃) are activities of titanium, hydrofluoric acid and nitric acid, respectively; and *l'*, *m'* and *n'* are orders of reaction for titanium, hydrofluoric acid and nitric acid, respectively.

Here is considered the time range where the reaction time is so short that *a*(HF) and *a*(HNO₃) can be regarded as practically chang-

ing little with the progress of the corrosion reaction. Assuming that these activities are equal to the hydrofluoric acid concentration and nitric acid concentration, respectively, the integral rate equation that corresponds to Eq. (2) is as follows:

$$X = [k \cdot C(\text{HF})^{m'} \cdot C(\text{HNO}_3)^{n'}] \cdot t = \alpha \cdot t \quad \dots(3)$$

$$\alpha = k \cdot C(\text{HF})^{m'} \cdot C(\text{HNO}_3)^{n'} \quad \dots(4)$$

where $C(\text{HF})$ and $C(\text{HNO}_3)$ are the hydrofluoric acid concentration and nitric acid concentration in the nitric-hydrofluoric solution, respectively. Common log values are taken of both sides of Eq. (3) as follows:

$$\log X = \log \alpha + \log t \quad \dots(5)$$

When the slope of the linear relationship between $\log t$ and $\log X$ is obtained, it varies in the approximate range of 0.8 to 1.1, but close to 1.

Assuming that the immersion time dependence of the corrosion loss of titanium is not affected by the solution temperature, hydrofluoric acid concentration, and nitric acid concentration, the mean value of the slope S of the linear relationship and its 95% confidence interval are as given by

$$\text{Mean value of } S = 0.938335 \pm 0.039093 \quad \dots(6)$$

This variation is 4.17% of the mean value of S , and it is judged practically possible to approximate S by its mean value. When the solution temperature, hydrofluoric acid concentration, and nitric acid concentration are constant, the corrosion loss X of titanium can be approximated as a function of the immersion time by

$$\log X \doteq \log \alpha + 0.938 \cdot \log t \quad \dots(7)$$

3.2 Dependence of corrosion loss on hydrofluoric acid concentration and nitric acid concentration

Fig. 3 shows double logarithmic plots by immersion time of the effects of the hydrofluoric acid concentration $C(\text{HF})$ and nitric acid concentration $C(\text{HNO}_3)$ on the corrosion loss X of titanium in the nitric-hydrofluoric acid solutions at different temperatures. When the nitric acid concentration is constant, the logarithmic corrosion loss linearly increases with increasing logarithmic hydrofluoric acid concentration, regardless of the solution temperature and immersion time. When the hydrofluoric acid concentration is constant, the nitric acid concentration dependence of the corrosion loss of titanium in the nitric-hydrofluoric acid solution is very small. The corrosion loss of titanium in the nitric-hydrofluoric acid solution is considered to practically depend on the hydrofluoric acid concentration. When common logarithmic values of both sides of Eq. (3) are taken and arranged by considering the results of Eq. (7), the following equations are obtained:

$$\log X = \log \beta + m' \cdot \log C(\text{HF}) \quad \dots(8)$$

$$\beta = k \cdot t^{0.938} \cdot C(\text{HNO}_3)^{n'} \quad \dots(9)$$

$$\log X = \log \gamma + n' \cdot \log C(\text{HNO}_3) \quad \dots(10)$$

$$\gamma = k \cdot t^{0.938} \cdot C(\text{HF})^{m'} \quad \dots(11)$$

Assuming that the hydrofluoric acid concentration dependence and nitric acid concentration dependence of the corrosion loss of titanium in the nitric-hydrofluoric acid solution are affected little by the solution temperature and immersion time on the basis of Eqs. (8) and (10), m' and n' are obtained from Fig. 3 as follows:

$$m' = 0.926 \pm 0.027 \quad \dots(12)$$

$$n' = 0.042 \pm 0.025 \quad \dots(13)$$

The hydrofluoric acid concentration dependence and nitric acid concentration dependence of the corrosion loss of titanium in the experimental concentration ranges are thus approximated by

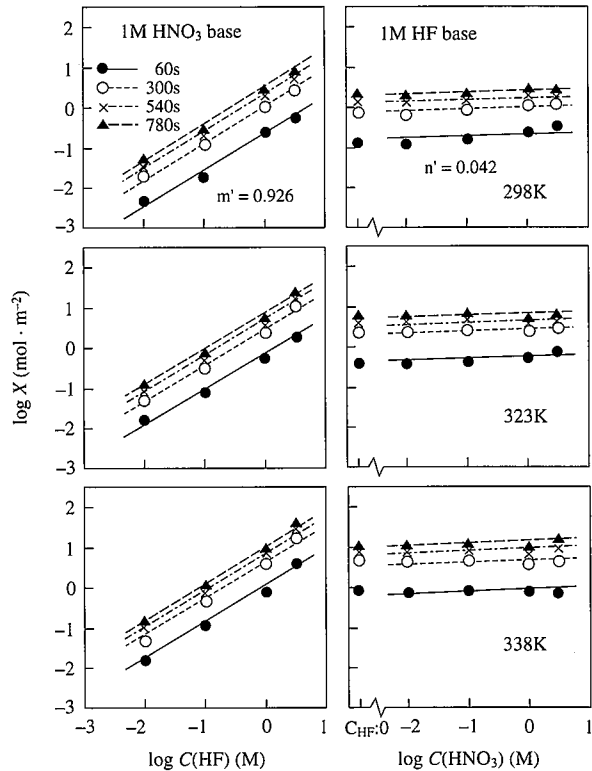


Fig. 3 Effects of HF concentration and HNO_3 concentration on corrosion loss X of titanium

$$\log X \doteq \log \beta + 0.926 \cdot \log C(\text{HF}) \quad \dots(14)$$

$$\log X \doteq \log \gamma + 0.042 \cdot \log C(\text{HNO}_3) \quad \dots(15)$$

3.3 Solution temperature dependence of corrosion loss

Fig. 4 shows Arrhenius plots of the effect of the solution temperature on the corrosion loss of titanium in the nitric-hydrofluoric acid solution as distinguished by the immersion time, hydrofluoric acid concentration, and nitric acid concentration. Regardless of the immersion time, hydrofluoric acid concentration, and nitric acid concentration, the logarithmic corrosion loss decreases almost linearly as the reciprocal of the absolute temperature increases, and an Arrhenius equation holds. The rate constant k in Eq. (3) is given by

$$k = A' \cdot \exp(-E_a / RT) \quad \dots(16)$$

where A' and E_a are the apparent frequency factor and activation energy ($\text{J} \cdot \text{mol}^{-1}$), respectively; R is the gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); and T is the absolute temperature (K).

Given the results of Eq. (7), Eqs. (17) and (18) are derived from Eq. (3) and (6).

$$\log X = \log \delta - (E_a / 2.303RT) \quad \dots(17)$$

where d is

$$\delta = A' \cdot t^{0.938} \cdot C(\text{HNO}_3)^{0.042} \cdot C(\text{HF})^{0.926} \quad \dots(18)$$

According to Eq. (17), the slope of the linear relationship between $\log X$ and $1/T$ is obtained from Fig. 4. The slope ($E_a / 2.303R$) of the linear relationship between $\log X$ and $1/T$ is practically constant despite the changes in the immersion time, hydrofluoric acid concentration, and nitric acid concentration. The average apparent activation energy is obtained as follows:

$$E_a = 33190 \pm 1273 \text{ J} \cdot \text{mol}^{-1} \quad \dots(19)$$

The above experimental results indicate that when the immer-

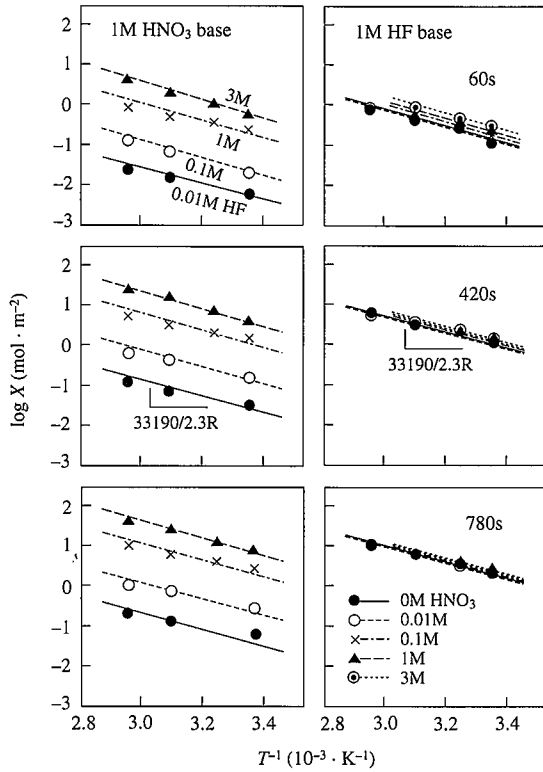


Fig. 4 Effect of solution temperature on corrosion reaction of titanium (Arrhenius plots)

tion time, hydrofluoric acid concentration, and nitric acid concentration are constant, the solution temperature dependence of the corrosion loss of titanium is approximated by

$$\log X \doteq \log \delta - (33190 / 2.303RT) \quad \dots(20)$$

From Eqs. (18) and (20), the mean value of the logarithmic apparent frequency factor, or $\log A'$, and the 95% confidence interval are obtained as given by

$$\text{Mean value of } \log A' = 3.400 \pm 0.152 \quad \dots(21)$$

3.4 Integral rate equation of titanium in nitric-hydrofluoric acid solution

The above-mentioned effects of the immersion time, nitric acid concentration, hydrofluoric acid concentration, and solution temperature on the corrosion loss of titanium in the nitric-hydrofluoric acid solution can be finally derived from the experimental equations (7), (14), (15), (20), and (21). The results obtained are given in Eq. (22), and the mean values, 95% confidence intervals, and significance levels of the constants and factors are listed in **Table 1**.

$$\log X \doteq \log A' - (E_a / 2.303RT) + m' \cdot \log C(\text{HF}) + n' \cdot \log C(\text{HNO}_3) + S \cdot \log t \quad \dots(22)$$

$(T/K, R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$

Table 1 Statistical analysis results of various parameters

	Mean value	95% confidence interval	Significance level
$\log A'$	3.400	± 0.152	4.47%
E_a	33190	± 1273	3.84%
B'	0.926	± 0.027	2.92%
C'	0.042	± 0.025	59.52%
S	0.938	± 0.039	4.16%

For the purpose of clarifying errors in the observed values and calculated values, **Fig. 5** shows the correlation between the corrosion loss ($\log X_{\text{calcu.}}$) calculated by substituting the results of Table into Eq. (22) and the corrosion loss ($\log X_{\text{obs.}}$) observed in the experiment. The coefficient of determination (R^2) that describes the correlation between $\log X_{\text{calcu.}}$ and $\log X_{\text{obs.}}$ is a very high 0.983. It is judged fully possible to estimate the corrosion loss of titanium in the nitric-hydrofluoric acid solution by using Eq. (22).

In **Fig. 6**, the observed values (indicated by the respective symbols) of the corrosion loss of titanium in the nitric-hydrofluoric acid solution at a temperature of 323K after an immersion time of 360 s as measured separately from the corrosion loss data used to derive Table 1 and Eq. (22) are compared with the calculated values (indicated by the broken lines) of the corrosion loss of titanium as determined using Table 1 and Eq. (22). The observed values agree very well with the calculated values, and the results of comparison are

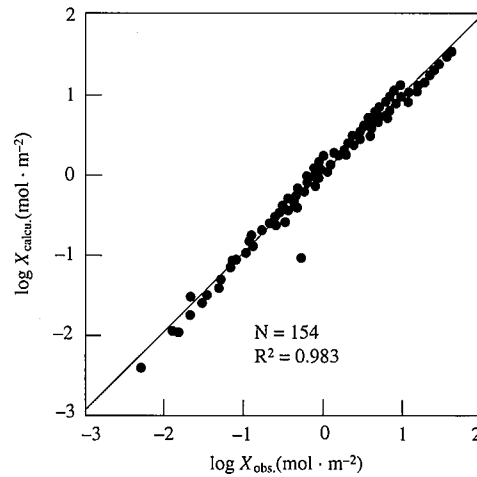


Fig. 5 Correlation between observed values and calculated values of corrosion loss X of titanium

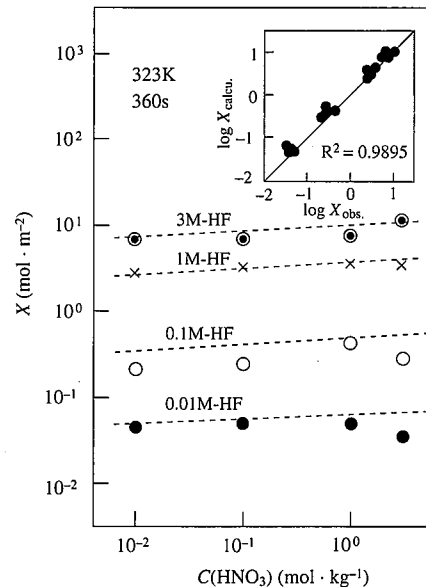


Fig. 6 Effect of HNO_3 concentration on corrosion loss X of titanium in various HNO_3/HF solutions (observed values indicated by symbols and calculated values indicated by dotted lines)

also good. This means that the corrosion loss of titanium in nitric-hydrofluoric acid solutions with nitric acid concentrations of 0 to 3 mol · kg⁻¹ and hydrofluoric acid concentrations of 0.01 to 3 mol · kg⁻¹ in the temperature range of 298 to 338K can be estimated by using Table 1 and Eq. (22).

4. Conclusions

- 1) The effects of the immersion time, nitric acid concentration, and hydrofluoric acid concentration on the corrosion loss of titanium in nitric-hydrofluoric acid solutions with different nitric and hydrofluoric acid concentrations were studied. It was found that the corrosion loss of titanium increases with increasing immersion time, hydrofluoric acid concentration and temperature and that the effect of the nitric acid concentration on the corrosion loss of titanium is small.
- 2) The following equation was derived as practical equation for estimating the integral corrosion rate of titanium in the nitric-hydrofluoric acid solution:

$$\log X = \log A' - (E_a / 2.303RT) + m' \cdot \log C(\text{HF}) + n' \cdot \log C(\text{HNO}_3) + S \cdot \log t$$

The mean values and 95% confidence intervals of these constants and coefficients were obtained as follows:

$$\log A' = 3.400 \pm 0.152$$

$$E_a = 33190 \pm 1273$$

$$m' = 0.926 \pm 0.027$$

$$n' = 0.042 \pm 0.025$$

$$S = 0.938 \pm 0.039$$

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